

Claim Rejection Under 35 U.S.C. § 112

Claims 5, 9, 13, and 38 have been rejected under 35 U.S.C. § 112, first paragraph, as containing subject matter which was not described in the specification in such a way to enable one skilled in the art to make and/or use the invention. The Office Action states that applicants fail to disclose “the derivatives of collagen and gelatin” in claim 5, “derivatives of alkoxyated derivatives” in claim 9, and “polysaccharide derivative” in claims 13 and 38.

Applicants point out that the Specification on page 7, beginning at line 17, discuss the polymers of particular utility used to impart water-soluble / water-dispersible characteristics to the carrier of claim 5 which states: “Polymers of polyvinyl alcohols, polyvinyl pyrrolidone, *proteins such as gelatin and collagen and derivatives thereof*, or carbohydrates such as arabinogalactan have been recognized as having particular utility.” Collagen derivatives are well known in the art. See International Cosmetic Ingredient Dictionary and Handbook, Vol. 3 (9th ed. 2002). Further, as discussed in the Encyclopedia of Chemical Technology, (Vol. 12, page 406), gelatin is a derived protein obtained by partial hydrolysis of collagen. Therefore, gelatin itself is a collagen derivative. Gelatin derivatives produced by modifying the chemically active groups on gelatin molecules are similarly known in the art. See Encyclopedia of Chemical Technology, Vol. 12, page 414 (1997).

Applicants note that Claim 9, which depends from claim 7, gives specific examples of plasticizers used in the carrier of the present invention which are discussed in the Specification on page 8, line 7 as follows:

Suitable plasticizers for use in the present invention include, but are not limited to, polyhydric alcohols such as glycerin, polyglycerol, alkyl polyglycosides, diethylene glycol, triethylene glycol, polyethylene glycol, random copolymers of ethylene oxide and propylene oxide, ethylene oxide/propylene oxide block copolymers such as those available from BASF under the Pluronic tradename, propylene glycol, sorbitol, sorbitol esters, butanediol, *and their alkoxyated derivatives . . .*

Both the Specification and claim 9 contain the same language, disclosing a list of suitable compounds and their alkoxyated derivatives for use as plasticizers. As known by those skilled in the art, typical alkoxyated derivatives are addition reaction products of oxirane compounds with alcohols, *alkoxyated* with alkylene oxide, typically

ethylene oxide and/or propylene oxide. See generally Encyclopedia of Chem. Vol. 23, page 507 (1997).

In claims 13 and 38, specific examples of polymer for use in the water-soluble/water-dispersible adhesive layer are claimed. The Specification on page 11, beginning at line 1, discloses the following: "Polymers suitable for use in the adhesive include, but are not limited to, poly(ethylene oxide); *natural and synthetic polysaccharides and their derivatives . . .*" As discussed in the Encyclopedia of Chemical Technology, (Vol. 4, page 932) polysaccharides are the most abundant form of carbohydrates, and contain glycosyl units with unsubstituted hydroxyl groups available for esterification or etherification. Polysaccharide derivatives are further defined by their degree of substitution. Thus, those skilled in the art would know or could easily determine polysaccharides, and their derivatives, for use in the present invention by the substituted groups on the glycosyl units.

The Applicants respectfully assert that the Specification contains an enabling scope of compounds for use in the present invention. Further, those skilled in the art would know or could determine the derivatives mentioned above in light of the water-soluble / water-dispersible requirements of the carrier and the adhesive in the present invention. Thus, Applicants respectfully request that the rejections under 35 U.S.C. § 112 be withdrawn.

Claim Rejections Under 35 U.S.C. § 103(a)

Claims 1-39 are rejected under 35 U.S.C. § 103(a) as obvious over Garbe (USPN 5,688,523) in view of Scholz (USPN 6,019,997). The Examiner states that Garbe teaches an adhesive sheet material composed of "a water-soluble carrier comprising addition polymers (e.g. acrylates)," liquid excipients "which can read on plasticizers," and "a backing film." The Examiner acknowledges that Garbe does not teach an active agent, and relies on Scholz for that disclosure.

Applicants respectfully traverse the rejection. The present rejection of the pending claims does not set forth a case of *prima facie* obviousness. Referring to §706.02(j) of the M.P.E.P, a rejection under 35 U.S.C. §103 should set forth in the Office Action:

- (1) the relevant teachings of the prior art relied upon;

- (2) the difference(s) or differences in the claim over the applied reference(s);
- (3) the proposed modification of the applied reference(s) necessary to arrive at the claimed subject matter; and
- (4) an explanation of why such proposed modification would have been obvious to one of ordinary skill in the art at the time the invention was made.

Further, this same section of the M.P.E.P. states that to establish a prima facie case of obviousness, three basic criteria must be met:

- (1) there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings;
- (2) there must be a reasonable expectation of success;
- (3) the prior art reference (or references when combined) must teach or suggest all the claim limitations.

Moreover, the teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on Applicants' disclosure.

With regard to the rejection, it is unclear, for example, why all of the modifications necessary to provide Applicants' claimed invention would have been obvious to one of ordinary skill in the art at the time the invention was made (or even at the time the application was filed) absent the use of Applicants' application (e.g., is not clear why one of ordinary skill in the art would try to obtain a delivery device for an active agent that is water-soluble when placed on skin), that the result would be Applicants' invention, or that all the features in the claims are disclosed in, or suggested by, the references relied upon.

The Office Action fails to point out any teaching in Garbe to water-solubility of the polymers, or the pressure sensitive adhesive as disclosed therein. Garbe discloses neither the water-soluble / water-dispersible carrier nor the water-soluble / water-dispersible adhesive of the present invention. Rather, Garbe teaches a method of manufacturing a pressure sensitive sheet with layers that lack the characteristics of the present invention, namely water-solubility or water-dispersibility. In specifying the

polymers for use in Garbe's disclosure, Garbe incorporates by reference the polymers listed in U.S. Patent No. 4,732,808 to Krampe (column 9, lines 50-57) and silicone polymers listed in U.S. Patent No. 5,232,702 to Pfister. The polymers listed in Krampe and Pfister are water-insoluble. Further, suitable backing layers listed in Garbe (column 3, lines 30-40) are also water insoluble.

Garbe, and the patents Garbe incorporates by reference, are concerned with transdermal delivery devices that provide pervasive adhesion on skin without excessive residue or adhesion loss (col. 1, lines 15-23; col. 5, lines 36-62). The patent does not teach or suggest a combination of layers, each layer capable of dissolving or dispersing once in contact with water. In contrast to the Office Action's characterization of the reference, Garbe lacks any discussion of the water-solubility of the polymer layers or the pressure sensitive sheet formed after constructing the layers together.

Rather, the cited reference teaches away from water-solubility in a drug delivery device. Garbe specifies that the pressure sensitive sheet material contain a coating medium "not more than that amount which causes the product pressure sensitive adhesive sheet material to lose adhesion or leave substantial residue on the skin when peeled from the skin." Moreover, the liquid excipients used in the coating medium or described as "oily materials" capable of phase separating from the continuous phase when added in excessive amounts to form an "oily layer that reduces adhesion of an otherwise adhesive matrix." See col. 4, lines 47-49; col. 6, lines 58-65. For at least these reasons, Garbe fails to disclose all the elements of the present invention to establish a *prima facie* case of obviousness.

Secondary Reference

Scholz fails to cure the deficiencies of Garbe. Scholz discloses a hydroalcoholic composition for transdermal delivery of a pharmaceutical agent. Scholz fails to teach or disclose a water soluble/water dispersible carrier layer or a water soluble/water dispersible adhesive layer, and only discloses use of the hydroalcoholic composition with transdermal delivery devices known in the art. Moreover, Garbe teaches that the polymers be soluble in the "only" liquid excipients. There is no teaching or suggestion in Scholz that the hydroalcoholic compositions disclosed therein would be soluble in the polymers in Garbe for coating on a substrate. Thus, the combination of Garbe and Scholz fails to teach all elements of the present invention.

Garbe fails to disclose water-soluble polymer layers either alone or in combination with Scholz. Applicants request that the rejections under 35 U.S.C. § 103(a) should be withdrawn.

Conclusion

In view of the arguments and amendments offered herein, Applicants respectfully submit that the Examiner's grounds for objection and rejection are overcome and respectfully solicit reconsideration and withdrawal of the rejections to place the application in condition for allowance.

| | |
|-------------------------------|------------------------------------|
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Respectfully submitted,

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| Technical/Trade Name | INCI Name | Technical/Trade Name | INCI Name |
|---|--|--|--|
| Coleus Scutellarioides Extract | Coleus Scutellarioides (or) Coleus Scutellarioides Extract | Collagens, Lauroyl Derivs. | Lauroyl Hydrolyzed Collagen |
| Colhibin (Pentapharm/Centerchem) | Hydrolyzed Rice Protein | Collagens, Lauroyl Derivs., Sodium Salts | Sodium Lauroyl Hydrolyzed Collagen |
| Colic Root Extract | Dioscorea Villosa (Wild Yam) Root Extract | Collagens, Myristoyl Derivs., Compds. with Triethanolamine | TEA-Myristoyl Hydrolyzed Collagen |
| Colladerm Procollagene SC (Biomex) | Soluble Collagen | Collagens, Palmitoyl Derivs. | Palmitoyl Hydrolyzed Collagen |
| Colla-Gel AC (Maybrook) | Gelatin | Collalift (Coletica/Bioetica, Inc.) | Hydrolyzed Malt Extract |
| Collagel S 100 (Seporga) | Soluble Collagen (and) Hydrolyzed Collagen | Collamino 25 (Brooks) | Collagen Amino Acids |
| Collagen | Collagen | Collamino Complex (Brooks) | Collagen Amino Acids (and) Acetamide MEA |
| Collagen Amino Acids | Collagen Amino Acids | Collamino Complex ESC (Brooks) | Collagen Amino Acids (and) Acetamide MEA (and) Hydrolyzed Elastin (and) Propylene Glycol (and) Hydrolyzed Silk |
| Collagen Amino Acids SF (ChemMark) | Collagen Amino Acids | Collamino Complex S (Brooks) | Collagen Amino Acids (and) Acetamide MEA (and) Propylene Glycol (and) Silk Amino Acids |
| Collagen-CCK-Complex (Kelisema Italy) | Soluble Collagen (and) Potassium Cocoate | Collamino Complex SS (Brooks) | Hydrolyzed Collagen (and) Hydrolyzed Silk (and) Acetamide MEA (and) Propylene Glycol |
| Collagen CLR (Chemisches Laboratorium) | Soluble Collagen | Collamino 40-SF (Brooks) | Collagen Amino Acids |
| Collagen Complex (Maybrook) | Soluble Collagen | Collamoist CG (Brooks) | Glyceryl Collagenate |
| Collagene 30% (Sinerga) | Hydrolyzed Collagen | Collamoist WS (Brooks) | Propylene Glycol (and) Hydrolyzed Collagen (and) PPG-12-PEG-65 Lanolin Oil |
| Collagen Extract | Collagen Extract | Collamoist ZN (Brooks) | Zinc Hydrolyzed Collagen |
| Collagen Fiber | Collagen | Collaplant (Bio-Dell) | Hydrolyzed Maple Sycamore Protein |
| Collagen-Hyaluronic Acid-Jelly (Labopharma) | Soluble Collagen (and) Sodium Hyaluronate | Collaplex 0.3 (GfN) | Soluble Collagen |
| Collagen Hydrolysate | Hydrolyzed Collagen | Collaplex 1.0 (GfN) | Soluble Collagen |
| Collagen Hydrolysate 30% (Pentapharm/Centerchem) | Hydrolyzed Collagen | Colla-Quat C (Maybrook) | Cocodimonium Hydroxypropyl Hydrolyzed Collagen |
| Collagen, Hydrolysates, Reaction Products with Capryloyl Chloride | Capryloyl Hydrolyzed Collagen | Colla-Quat PT (Maybrook) | Propyltrimonium Hydrolyzed Collagen |
| Collagen Hydrolyzate Cosmetic 50 (Maybrook) | Hydrolyzed Collagen | Collaron (GfN) | Atelocollagen |
| Collagen Hydrolyzate Cosmetic 55 (Maybrook) | Hydrolyzed Collagen | Collasol (Croda Oleochemicals) | Soluble Collagen |
| Collagen Hydrolyzate Cosmetic N-55 (Maybrook) | Hydrolyzed Collagen | Collasol (Croda, Inc.) | Soluble Collagen |
| Collagen Hydrolyzate Cosmetic SD (Maybrook) | Hydrolyzed Collagen | Collasol M (Croda, Inc.) | Soluble Collagen |
| Collagen-IMZ-Complex (Kelisema Italy) | Soluble Collagen (and) Sodium Cocoamphoacetate | Colla-Tein A-SD (Maybrook) | Hydrolyzed Collagen |
| Collagen-LSS-Complex (Kelisema Italy) | Soluble Collagen (and) Sodium Lauryl Sulfate | Colla-Tein Collagen Mask (Maybrook) | Soluble Collagen (and) Collagen |
| Collagenna (Ennagram) | Water (and) Spotted Dogfish Skin Extract | Colla-Tein N-35 (Maybrook) | Hydrolyzed Collagen |
| Collagen Nativ, 1% (Crodarom) | Soluble Collagen | Collinsonia Canadensis | Collinsonia Canadensis (or) Collinsonia Canadensis Extract (or) Collinsonia Canadensis Root |
| Collagen Native Extra 1% (Maybrook) | Soluble Collagen | Collinsonia Canadensis Extract | Collinsonia Canadensis (or) Collinsonia Canadensis Extract |
| Collagenol LS/HC-10 (Serobiologiques) | Hydrolyzed Collagen | Collinsonia Canadensis Root | Collinsonia Canadensis (or) Collinsonia Canadensis Root |
| Collagenon (Vevy) | Hydrolyzed Collagen | Collodex (Dextran) | Lauroyl Hydrolyzed Collagen |
| Collagen P (Provital/Centerchem) | Hydrolyzed Collagen | Collodion | Collodion |
| Collagen Powder (Brooks) | Collagen | Collodion, Flexible | Flexible Collodion |
| Collagen Powder 100 (Nonogawa) | Collagen | Colloidal Kaolin NF-Bacteria Controlled (Whittaker, Clark & Daniels) | Kaolin |
| Collagen-Protein WN (Cosmetochem) | Hydrolyzed Collagen | Colloidal Oatmeal | Colloidal Oatmeal |
| Collagen S (Provital/Centerchem) | Hydrolyzed Collagen | Colloidal Sulfur | Colloidal Sulfur |
| Collagen S.D. (Tri-K) | Collagen | | |
| Collagen Sheet | Collagen | | |

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VOLUME 12

**FUEL RESOURCES
TO
HEAT STABILIZERS**



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GELATIN

Gelatin [9000-70-80] is a protein obtained by partial hydrolysis of collagen, the chief protein component in skin, bones, hides, and white connective tissues of the animal body (see PROTEINS). Type A gelatin is produced by acid processing of collagenous raw material; type B is produced by alkaline or lime processing. Because it is obtained from collagen by a controlled partial hydrolysis and does not exist in nature, gelatin is classified as a derived protein. Animal glue and gelatin hydrolysate, sometimes referred to as liquid protein, are products obtained by a more complete hydrolysis of collagen and thus can be considered as containing lower molecular-weight fractions of gelatin.

Use of animal glues was first recorded ca 4000 BC in ancient Egypt (1). Throughout subsequent centuries, glue and crude gelatin extracts with poor organoleptic properties were prepared by boiling bone and hide pieces and allowing the solution to cool and gel. Late in the seventeenth century, the first commercial gelatin manufacturing began. At the beginning of the nineteenth century, commercial production methods gradually were improved to achieve the manufacture of high molecular weight collagen extracts with good quality that form characteristic gelatin gels (1-3).

Uses of gelatin are based on its combination of properties; reversible gel-to-sol transition of aqueous solution; viscosity of warm aqueous solutions; ability to act as a protective colloid; water permeability; and insolubility in cold water, but complete solubility in hot water. It is also nutritious. These properties are utilized in the food, pharmaceutical, and photographic industries. In addition, gelatin forms strong, uniform, clear, moderately flexible coatings which readily swell and absorb water and are ideal for the manufacture of photographic films and pharmaceutical capsules.

Chemical Composition and Structure

Gelatin is not a single chemical substance. The main constituents of gelatin are large and complex polypeptide molecules of the same amino acid composition as the parent collagen, covering a broad molecular weight distribution range. In the parent collagen, the 18 different amino acids are arranged in ordered, long chains, each having ~95,000 mol wt. These chains are arranged in a rod-like, triple-helix structure consisting of two identical chains, called α_1 , and one slightly different chain called α_2 (4-6). These chains are partially separated and broken, ie, hydrolyzed, in the gelatin manufacturing process. Different grades of gelatin have average molecular weight ranging from ~20,000 to 250,000 (7-14). Molecular weight distribution studies have been carried out by fractional precipitation with ethanol or 2-propanol and by complexing with anionic detergent molecules. The coacervates are isolated and recovered as gelatin fractions (15-17).

Analysis shows the presence of amino acids from 0.2% tyrosine to 30.5% glycine (see AMINO ACIDS). The five most common amino acids are glycine [56-40-6], 26.4-30.5%; proline [147-85-3], 14.8-18%; hydroxyproline [51-35-4], 13.3-14.5%, glutamic acid [56-86-0], 11.1-11.7%; and alanine [56-41-7],

Gelatin is also used in so-called subbing formulations to prepare film bases such as polyester, cellulose acetate [9004-35-7], cellulose butyrate, and polyethylene-coated paper base for coating by aqueous formulations. Solvents such as methanol [67-56-1], acetone [67-64-1], or chlorinated solvents are used with small amounts of water. Gelatin containing low ash, low grease, and having good solubility in mixed solvents is required for these applications (see COATINGS). In certain lithographic printing, light-sensitive dichromated gelatin is used. Light causes permanent cross-linking of gelatin in the presence of the dichromate; this phenomenon is used to make relief images for printing. Dichromated gelatin coatings are commonly used in production of high quality holographic images. In this application, the light sensitivity of the image-receiving medium is less important than the image-resolving power (73). Gelatin coatings in photographic products are further tested for brittleness, scratch resistance, friction, swelling rate, drying rate, curling tendency, dry adhesion, wet adhesion, and pressure sensitivity. These properties are becoming more critical with the development of more sophisticated cameras and printing and processing equipment. Photographic technology offers a rapidly changing, highly sophisticated, very competitive market for photographic gelatin manufacturers.

Derivatized Gelatin. Chemically active groups in gelatin molecules are either the chain terminal groups or side-chain groups. In the process of modifying gelatin properties, some groups can be removed, eg, deamination of amino groups by nitrous acid [10024-97-2] (74), or removal of guanidine groups from arginine [74-79-3] by hypobromite oxidation (75); the latter destroys the protective colloid properties of gelatin. Commercially successful derivatized gelatins are made mostly for the photographic gelatin and microencapsulation markets. In both instances, the amino groups are acylated. Protein detergent is made by lauroylating gelatin. Phthalated gelatin is now widely used in the photographic industry (76). Arylsulfonylated gelatin has been patented for microencapsulation (qv) (77). Carbamoylated gelatin, made by treating gelatin with cyanate or nitrourea in neutral aqueous solution, is also used by the photographic industry (19,78-80). Active double bonds react with the amino groups in gelatin, and acrylic polymers have been grafted to gelatin (81). Gelatin has been derivatized by epoxides (82), cyclic sulfones (83), and cyanamide [420-04-2] (84). Cross-linking or hardening of gelatin attacks the same active groups, but an agent with two active sites is needed, eg, divinylsulfone [77-77-0], bis(isomaleimide) [13676-54-5], aziridines, bisepoxides, epichlorohydrin [106-89-8], polyisocyanates, and dichlorotriazine. Aldehydes such as formaldehyde [50-00-0] and glyoxal [107-22-2] are still used and to a small extent even potassium chromium alum [7788-99-0], $\text{Cr}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, and potassium aluminum alum [7784-24-9], $\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$.

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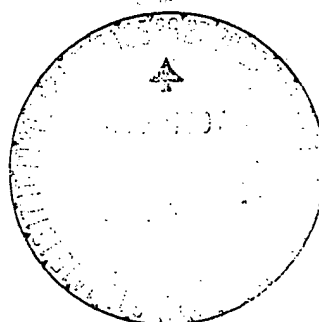
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VOLUME 23

SUGAR
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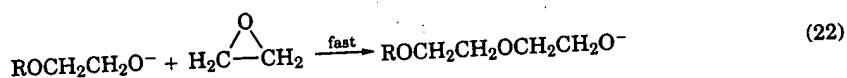
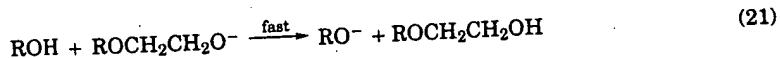
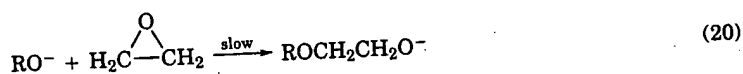
ethoxylates, the HLB number may be calculated from the following:

$$\text{HLB} = E/5$$

where E is the weight percentage of ethylene oxide in the molecule. The functionality of nonionic surfactants depends on HLB as follows:

| HLB range | Application |
|-----------|-------------------------------|
| 3-6 | water-in-oil (w/o) emulsifier |
| 7-9 | wetting agent |
| 8-15 | oil-in-water (o/w) emulsifier |
| 13-15 | detergent |
| 15-18 | solubilizer |

Ethoxylation. Base-catalyzed ethoxylation of aliphatic alcohols, alkylphenols, and fatty acids can be broken down into two stages: formation of a monoethoxy adduct and addition of ethylene oxide to the monoadduct to form the polyoxyethylene chain. The sequence of reactions is shown in equations 20-22:



Equation 20 is the rate-controlling step. The reaction rate of the hydrophobes decreases in the order primary alcohols > phenols > carboxylic acids (84). With alkylphenols and carboxylates, buildup of polyadducts begins after the starting material has been completely converted to the monoadduct, reflecting the increased acid strengths of these hydrophobes over the alcohols. Polymerization continues until all ethylene oxide has reacted. Beyond formation of the monoadduct, reactivity is essentially independent of chain length. The effectiveness of ethoxylation catalysts increases with base strength. In practice, ratios of 0.005-0.05:1 mol of NaOH, KOH, or NaOCH₃ to alcohol are frequently used.

Alcohol Ethoxylates. These products have emerged as the principal nonionic surfactants in consumer detergent products (Table 14). Consistent quality, expanding production capacity of relatively inexpensive detergent range straight-chain, highly biodegradable alcohols, and increasing usage in laundry products, particularly heavy-duty liquids, are the principal factors underlying this growth.

Alcohol ethoxylates vary in physical form from liquids to waxes. With increasing ethylene oxide content, viscosity increases; a slight hydrophobe odor, present in the lower members of the series, decreases; specific gravity increases

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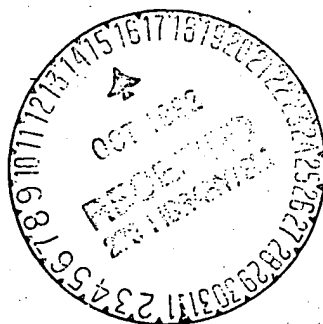
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VOLUME 4

BEARING MATERIALS
TO
CARBON



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Maltodextrins [9050-36-6] are mixtures of saccharides with average DE values of <20 (12). They are rather soluble, have a bland taste, and are widely used in foods. A dextrin is a product obtained by depolymerization of a polysaccharide.

Corn syrup solids are also dry products, have a smaller average size, and are comparatively sweeter (12). Both maltodextrins and corn syrup solids are used to prevent caking; enhance dispersibility and solubility; provide body or bulk; impart desirable texture; bind, carry, and protect flavors; control extrusion expansion; provide viscosity; form films and coatings; provide an oxygen barrier; inhibit crystallization; control sweetness; improve sheen; improve organoleptic characteristics; slow meltdown; and improve freeze-thaw stability.

Specifically prepared low DE starch products in the maltodextrin class, especially those from tapioca and potato starches, mimic a fatty mouthfeel and are used as fat replacers and/or spacers (see FAT SUBSTITUTES).

Another class of products are the cyclodextrins or cycloamyloses, a family of cyclic oligosaccharides containing α -D-glucopyranosyl units, most commonly seven (β -cyclodextrin [7585-39-9], cycloheptaamylose, cyclomaltoheptaose) (20,21). All members of this class of compounds are made by action of a specific enzyme, cyclodextrin glycosyltransferase [9030-09-5], on starch. In all, the glucosyl units are joined by (1 \rightarrow 4) glycosidic linkages to form a ring, the cavity of which is especially useful for the formation of inclusion complexes with hydrophobic guest molecules. These stable complexes are potentially useful in the food industry to provide stable flavors and fragrances in dry powder form, in the pharmaceutical industry, and in other applications where increased chemical and/or physical stability, solubility control, or controlled release is desired, for example, with agricultural chemicals (see INCLUSION COMPOUNDS).

More extensive depolymerization of starch yields syrups. Syrups are purified, concentrated, aqueous solutions of saccharides with an average DE value of >20. Enzymes are most often used to make syrups, although combinations of acid- and enzyme-catalyzed hydrolyses and complete acid conversion may be used. Syrups are grouped into subclasses. Some contain as little as 35% of maltooligosaccharides. The maltooligosaccharides are both linear and branched, the branched structures arising from amylopectin. Products with progressively higher concentrations of lower molecular weight products are progressively sweeter and less viscous. By using proper conditions, syrups with specific defined compositions, for example, high maltose syrups, are prepared. The annual consumption in the United States of corn syrups is >3,000,000 tons (80.3% solids basis).

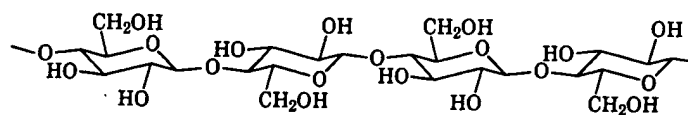
POLYSACCHARIDES

It has been estimated that >90% of the carbohydrate mass in nature is in the form of polysaccharides. In living organisms, carbohydrates play important roles. In terms of mass, the greatest amounts by far are structural components and food reserve materials, in that order and both in plants. However, carbohydrate molecules also serve as structural and energy storage substances in animals and serve a variety of other essential roles in both plants and animals.

Since polysaccharides are the most abundant of the carbohydrates, it is not surprising that they comprise the greatest part of industrial utilization (9,22).

Most of the low molecular weight carbohydrates of commerce are produced by depolymerization of starch. Polysaccharide materials of commerce can be thought of as falling into three classes: cellulose, a water-insoluble material; starches, which are not water-soluble until cooked; and water-soluble gums.

Cellulose. Cellulose [9004-34-6] (qv) is the principal cell wall component of higher plants and the most abundant polysaccharide. Approximately one-half the mass of perennial plants and one-third the mass of annual plants is cellulose. It is a high molecular weight, linear, insoluble polymer of repeating β -D-glucopyranosyl units joined by (1 \rightarrow 4) glycosidic linkages. Because of their linearity and stereoregular nature, cellulose molecules associate in extended regions, forming polycrystalline, fibrous bundles (23,24).



cellulose

High quality cellulose can be obtained from wood through pulping (delignification) and subsequent purification. The measure of the quality of cellulose is its content of alpha-cellulose, that portion insoluble in 18% alkali. Beta-cellulose is that portion which dissolves in 18% alkali, but precipitates when the solution is neutralized. Gamma-cellulose remains soluble after neutralization of the 18% alkali solution. The greatest amount of cellulose used is the purified, but not highly purified, wood pulp that is used in the manufacture of paper (qv), associated products, absorbants, rayons, and nonwovens. A number of derivatives of cellulose are also commercial entities. The water-soluble ones are covered later.

Every polysaccharide contains glycosyl units with unsubstituted hydroxyl groups available for esterification or etherification. Polysaccharide derivatives are described by their degree of substitution (DS), which is the average number of substituent groups per glycosyl unit. Because each monomeric unit of cellulose molecules has free hydroxyl groups at C-2, C-3, and C-6, the maximum DS for cellulose, and all polysaccharides composed exclusively of neutral hexosyl units, the majority of polysaccharides, is 3.0.

Several cellulose esters (qv) are prepared commercially. Cellulose xanthate [9032-37-5] is made by reaction of cellulose swollen in 8.5–12% sodium hydroxide solution (alkali cellulose [9081-58-7]) with carbon disulfide and is soluble in the alkaline solution in which it is made. When such a solution, termed viscose, is introduced into an acid bath, the cellulose xanthate decomposes to regenerate cellulose as rayon fibers or cellophane sheets (see FIBERS, REGENERATED CELLULOSES).

Cellulose acetate [9004-35-7], prepared by reaction of cellulose with acetic anhydride, acetic acid, and sulfuric acid, is spun into acetate rayon fibers by dissolving it in acetone and spinning the solution into a column of warm air that evaporates the acetone. Cellulose acetate is also shaped into a variety of plastic products, and its solutions are used as coating dopes. Cellulose acetate butyrate [9004-36-8], made from cellulose, acetic anhydride, and butyric anhydride in the presence of sulfuric acid, is a shock-resistant plastic.

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Cellulose nitrate (pyroxylin) [9004-70-0], made from cellulose and a mixture of nitric and sulfuric acids, is called gun cotton and is used in explosives. Nitrates of lower DS find some application in coatings and adhesives.

Ethylcellulose [9004-57-3], a cellulose ether (qv), as prepared commercially, ie, of high DS, is thermoplastic and has a low density (1.14 g/cm^3). It forms films of good thermostability and excellent flexibility and toughness. Ethylcellulose is used in lacquers, inks, and adhesives and is combined with waxes and resins in the preparation of hot-melt plastics. It is also used as a pharmaceutical tablet binder.

Treatment of cellulose with acids results in preferential hydrolysis in the more accessible amorphous regions and produces a product known as microcrystalline cellulose (MCC). MCC is used to prepare fat-free or reduced-fat food products, to strengthen and stabilize food foams, as a tableting aid, and as a noncaloric bulking agent for dietetic foods. It has GRAS status.

Hemicelluloses and Related Polysaccharides. Hemicelluloses [9034-32-6] are a large group of polysaccharides that are associated with cellulose in the primary and secondary cell walls of all higher plants, but otherwise have no relationship to cellulose (2). They are also present in some other plants.

Hemicelluloses (qv) are heteroglycans. They do not comprise a distinct class of chemical structures. Constituent monosaccharides are D-xylose, D-mannose, D-glucose, D-galactose, L-galactose [15572-79-9], L-arabinose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid [4120-73-4], D-galacturonic acid [685-73-4], and to a lesser extent L-rhamnose, L-fucose, and various methyl ethers of neutral sugars, with a limit of perhaps six different glycosyl units per molecule. Both woody and nonwoody tissues contain 20–35% hemicelluloses. Some are neutral polymers, but most are acidic. The most abundant have a xylan backbone, ie, a chain of (1→4)-linked β -D-xylopyranosyl units. The chain may be linear, but is often branched and usually contains short side chains whether basically linear or branched. The most common acidic hemicelluloses are O-acetylated (4-O-methyl-D-glucurono)xylans [9062-57-1] and L-arabino-(4-O-methyl-D-glucurono)xylans [69865-67-4, 9040-28-2, 98913-73-6], both often containing minor amounts of other sugar units as well. In the former, which are the preponderant hemicelluloses of woody angiosperms, the 4-O-methyl- α -D-glucopyranosyluronic acid units are most often joined to D-xylopyranosyl main chain units by (1→2) linkages. Some hemicelluloses have D-glucopyranosyluronic acid units as side chains, both the methylated and unmethylated forms in the same molecule being common. The number of uronic acid units varies considerably. Most hardwood xylans have approximately one uronic acid unit per 10 D-xylosyl units. The distribution is not uniform. Acetyl groups occur to the extent of 3–17%, with the greatest number being present in hardwood hemicelluloses.

The L-arabino-(4-O-methyl-D-glucurono)xylans are found in softwoods and annual plants. The L-arabinose is present primarily as α -L-arabinofuranosyl units, although β -L-arabinopyranosyl units may also be present. In either case, the arabinosyl units are often, but not always, present as single-unit side chains, as are the uronic acid units.

Cell walls of woods contain other subgroups of hemicelluloses, in particular those composed primarily of D-mannopyranosyl or D-galactopyranosyl units. Glucomannans [11078-31-2] comprise 3–5% of the wood of angiosperms and 3–12% of the wood of gymnosperms. Galactoglucomannans [9040-29-3] are also common.